Review

A personal account of some dinitrogen and organometallic chemistry research at the University of Sussex

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Abstract

This article reviews the development of dinitrogen chemistry and some associated organometallic chemistry at the University of Sussex with which the author was directly involved. The establishment of the basic heavy-element halide phosphine chemistry laid the ground for the discovery of dinitrogen complexes of rhenium, osmium, molybdenum and tungsten. From there, some of the first well-defined reactions of coordinated dinitrogen (especially protonation and alkylation) were discovered and the essential mechanisms of such reactions were established. This allowed the development of models for the action of nitrogenases that are still probably the best available. Later work has produced similar models in iron chemistry and a range of organometallic chemistry has been uncovered in the effort to discover parallels between the basic organometallic chemistry of substances such as metal carbonyls, dinitrogen complexes and hydrides in their interactions with acetylenes and cyclpropene.
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My interest in organometallic chemistry goes back to the early sixties. My doctorate work involved some coordination chemistry of silicon, germanium and titanium, and I attempted to research in organosilicon chemistry when I took up my first appointment at The University of Manchester Institute of Science and Technology (UMIST). During a sabbatical year with E.O. Fischer in Munich I undertook transition-metal organometallic research [1] and learned Schlenk techniques. I became entranced by the work being done in E.O.'s group, in which the first carbene complexes were then being characterised. I returned to UMIST but could not really get going in transition-metal work.

I became involved in dinitrogen chemistry in 1965, when I moved to the University of Sussex to take up a post in the Unit of Nitrogen Fixation. This Unit had been established by the then UK Agricultural Research Council under the aegis of Joseph Chatt. The remit of this Unit, which was unique in the spread of expertise it attracted, ranging from microbiologists through biochemists to inorganic chemists, was to determine the mechanism of biological nitrogen fixation. The biological programme was directed by John Postgate, and the Unit and its successor manifestations produced a stream of original and innovative discoveries for nearly 35 years, until it effectively ceased to exist in about 2000. These discoveries did not come easily, and, in the beginning, were slow to come at all. However, the chemists in particular were lucky to be settled at the University of Sussex where Colin Eaborn was cleverly constructing a Department of Chemistry that would rank amongst the best in the world, and not least in organometallic chemistry. We could not have had a warmer welcome.

When I arrived we were housed in one of the first chemistry laboratories to be built on the University of

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Sussex campus, though an even earlier arrival than myself, Ray Richards, fresh from his Ph.D., had already completed his first project, the design of our new building. Not many new graduates have had such a task thrust upon them, but Ray did it exceedingly well. As for research, there was no obvious place to start, and so Chatt decided that we should explore chemistry with elements that formed strong bonds to nitrogen, such as rhenium and osmium. This led us to look at rhenium nitrides, but scarcely had we started than Bert Allen described the first dinitrogen complex, $[Ru(NH_3)_5(N_2)]^{2+}$ [2]. I had repeated the preparation within two hours of receiving the paper, and things appeared even more disappointing from our personal point of view when it was reported shortly afterwards that the dinitrogen in this compound could be reduced to ammonia [3]. At about the same time Collman [4] described an iridium dinitrogen complex, and cobalt analogues [5] followed hard upon it. We were the Unit of Nitrogen Fixation, and several people asked pointed questions about what we were supposed to be doing now that the problem had been solved.

Fortunately for us, the situation was not quite as simple as it then appeared. Ray Richards and Jack Fergusson showed [6] that the dinitrogen reduction work was in error, probably due to contamination with hydrazine, and thereby established what became an absolutely essential requirement to identify genuine dinitrogen reductions, namely confirmation using ^{15}N. In any case, we were busy establishing and expanding the basic chemistry of tertiary phosphine complexes of some of the heavier, later transition metals [7], which turned out to be an essential basis for most of our subsequent work on dinitrogen complexes [8]. We also made some of the first studies of sharp NMR ^1H spectra in complexes exhibiting second-order paramagnetism [9]. In my own section of the Unit, Jon Dilworth was investigating the way in which rhenium compounds and hydrazines could produce nitrides, and amongst the hydrazines he used was dibenzoylhydrazine. This reacts with $[ReOCl_3(PPh_3)_2]$ to give a compound we termed "the green chelate" (Fig. 1). Even Chatt with his insistence on correct IUPAC nomenclature found it easier to use this name for it.
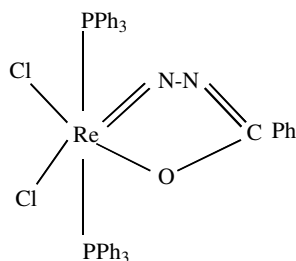
The green chelate proved to be a goldmine [10]. Jon found that reaction with methanol in the presence of further phosphines gave a series of dinitrogen complexes $[ReCl(N_2)(phosphine)_4]$, the first series of its kind. Rationalisation of the synthetic reaction was relatively easy (Fig. 2), though our discovery was fortuitous [11]. Related carbonyldinitrogen complexes soon followed [12]. A concerted effort showed that these complexes could act as donors towards Lewis acids, which was our first indication of characteristic dinitrogen reactivity [13].

Once we had the stoichiometric formula of the rhenium complexes, it was relatively easy to predict that reduction under dinitrogen of complexes $[OsCl_3(phosphine)_3]$, which we had earlier characterised, was likely to produce $[OsCl_2(N_2)(phosphine)_3]$, and so it proved [14]. The paper describing this new series of osmium dinitrogen complexes was accepted by Chemical Communications, though one referee, whose identity we could only guess at, ungraciously turned it down as "just another series of dinitrogen complexes".

At that stage none of these dinitrogen complexes with singly bound end-on dinitrogen seemed to show much real reactivity, but, in any case, we were much more interested in the biological metal, molybdenum, and, by extension, its congener, tungsten. Using the isoelectronic principle, after rhenium and osmium the obvious goal would clearly be complexes such as $[W(N_2)(phosphine)_5]$. This was indeed synthesised, but later and not by us [15] and we were beaten to the first molybdenum dinitrogen complexes $[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ and $[Mo(N_2)(Ph_3P)_2(CH_3C_6H_5)]$ [16], though neither of these have proved to be of as much value as the tungsten homologues of the diphosphine complex.

We subsequently prepared [17] further series of dinitrogen complexes, of the form $[M(N_2)_2(phosphine)_4]$, were M can be Mo or W, and the $(phosphine)_4$ can be of assemblages, monophosphines, diphosphines, and
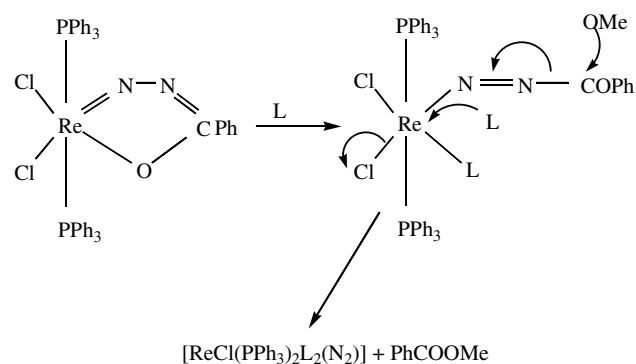

Fig. 1. The "green chelate".

Fig. 2. The preparation of the first rhenium(I) dinitrogen complexes. L may be a range of donors, including CO and tertiary phosphines, and many L also displace one or both PPh_3. The solvent is methanol.

triphosphines. Related carbonyls and hydrides were also obtained. Unfortunately these compounds did not seem to be very useful at first, indeed with the quasi-cyclobutane model for olefin metathesis as our guide we tried to make acetonitrile from dinitrogen and dimethylethyne with one of our bis(dinitrogen) complexes. We had an excited 24 h believing that the synthesis had actually worked, but then learned that the acetonitrile we had detected came from a dirty chromatograph syringe.

Somewhat later I suggested to Graham Heath that he might as well try to use [W(N$_2$)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] as a simple tungsten(0) compound and test some oxidative additions, such as others had uncovered with iridium(I). He chose to use acetyl chloride. Much to our surprise and delight the product turned out to be the first example of a well-defined complex containing a dinitrogen residue to be synthesised from a well-defined dinitrogen complex, namely [W(N$_2$COCH$_3$)Cl(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] [18]. The oxidative addition had indeed occurred, but it had taken place across the W–N≡N moiety. I should make clear that this was not the first reported reaction of coordinated dinitrogen, for others, such as Bercaw, Schrauzer and, above all, Shilov and Volpin, had produced ammonia and hydrazine from metal-mediated reductions of dinitrogen, but our system was clean and was amenable to mechanistic study. However, we assumed that we were observing attack by an electrophile on the basic dinitrogen, and consequently Ray Richards looked at the reaction of our dinitrogen complexes with protic acids.

Formally the results paralleled that from the dinitrogen acetylation, giving [W(NNH$_2$)Cl(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]$^+$ but they were much more significant. Using tungsten and molybdenum diphosphine complexes, he unravelled the first stages of dinitrogen protonation [19] and we showed later [20] that a third proton could be persuaded to attack the *exo*-nitrogen, a finding that was confirmed also by others (Fig. 3). Then, using monophosphine complexes, Ray showed that it was possible to protonate dinitrogen all the way to ammonia [21]. Unfortunately, such reactions resulted in the oxidation of the tungsten all the way from oxidation state zero to oxidation state six. The complex itself was completely destroyed, and could not be recycled. It was considerably later that Chris Pickett, also in the Unit, was able to use electrochemical techniques to make the W(diphosphine)$_2$ moiety the basis of a cyclic system for splitting the N–N bond to yield amines [22] and for converting dinitrogen to ammonia [23] (see below). In the meantime Shilov and his collaborators had developed very different catalytic systems that could convert dinitrogen to ammonia under protic conditions [24].

Our belief that electrophilic acylation and protonation were examples of the only type of reactivity exhibited by coordinated dinitrogen was soon shown to be wrong. Alex Diamantis copied Graham Heath's experiments with acetyl chloride, but using alkyl and aryl halides. This work showed that the coordinated dinitrogen could be alkylated [25], though arylation was not achieved by us and was found to be much rarer. Subsequently coordinated dinitrogen in these complexes has been silylated, germylated and stannylated [26], but the reactivity of coordinated dinitrogen with dihydrogen and silanes discovered much more recently by Fryzuk [27] occurs in very different compounds.

We carried on with our attempts to understand the olefin metathesis reaction, though these became hampered by the observation that our catalyst system could be explosive [28]. However, with Ray Haines we produced an often-cited review of the subject. A bit later we showed that acetylene metathesis also involves cleavage of the C–C triple bond and involved carbynes, though this was an expected extrapolation from the olefin chemistry [29]. At the same time we followed up the organometallic chemistry of further metals. The easy and safe synthesis of Cl$_2$PCH$_2$CH$_2$PCl$_2$ [30] was a considerable advance since it gave us access to a wide range of diphosphines, and we also worked with unsaturated substituents on others [31]. We reported new carbonylrhenium complexes [32], the synthesis of cyclopentadienyl carbonyls of niobium and tantalum [33], low-pressure syntheses of niobium carbonyls [34], and new cyclopentadienyltitanium compounds [35]. Our researches also threw up novel compounds, generally of molybdenum and tungsten, such as carbon dioxide complexes [36] and diazoalkane complexes [37], formato complexes [38], an hydroxycarbene complex [39], and bis(organodiazenido) compounds [40]. However, our major interest was always the study of the reactivity of coordinated dinitrogen and the organometal studies listed here tended to that end.

The alkylations of dinitrogen were shown to be essentially radical reactions, in the case of tungsten, but not molybdenum, being photo-activated, Fig. 4 [41]. Presumably the other Group 14 reactions are similarly radical reactions. This remains one of the only two completely characterised reaction pathways of coordinated dinitrogen. I still believe this reaction path at molybdenum to be essentially what occurs in the enzyme, though there is a substantial body of opinion that remains to be convinced. However, in the enzyme, protons and electrons must arrive at the dinitrogen at more or less the same time, maintaining an approximate electroneutrality and thus obviating the large change in oxidation state observed by Ray Richards in his protonations.
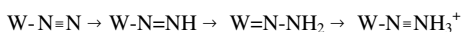
$$W\text{-}N{\equiv}N \rightarrow W\text{-}N{=}NH \rightarrow W{=}N\text{-}NH_2 \rightarrow W\text{-}N{\equiv}NH_3{}^+$$

Fig. 3. The initial stages in the protonation of dinitrogen coordinated end-on to tungsten.

$$N_2$$

(a)

$$M(N_2)_2 \longrightarrow M(N_2) \xrightarrow{RX} M(N_2)(XR)$$

$$M(N_2)X + R^{\cdot}$$

$$MX(N_2R_2)^+ \xleftarrow{RX} MX(N_2R) \longleftarrow$$

(b) SH

$$MX(N_2S) \longleftarrow S^{\cdot} + RH$$
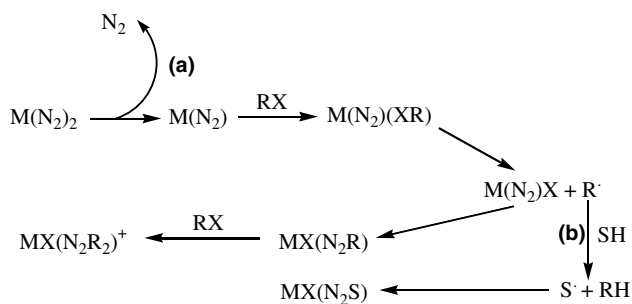
Fig. 4. The mechanistic pathways for the alkylation of dinitrogen coordinated to Mo or W. M = Mo or W. (a) This reaction requires light activation for M = W. (b) This occurs with an aryl halide and a solvent (SH) such as THF.

The discovery of mono- and di-alkylated species enabled us to undertake electrochemistry on them, something we could not initially undertake with the protonated species indicated in Fig. 3. The advantage of this was that we were able to mimic more closely the type of reactivity that we thought must occur if the enzyme reduction of dinitrogen happens at molybdenum. Chris Pickett and Wasif Hussain [22] showed that, under appropriate conditions one could reduce the dialkylated species, and that addition of acid then finally split the N–N bond to produce a nitrido species, which was fully characterised, as well as a secondary amine (Fig. 5). The protonation of nitrido complexes to yield ammonia had long been known, for example in osmium chemistry, so that we were able to delineate a complete pathway from dinitrogen to ammonia in individual steps (Fig. 6), as well as opening a route from dinitrogen to secondary amines.

Richard Henderson investigated the mechanisms of the protonation reactions of coordinated dinitrogen in our phosphine complexes using stopped-flow techniques, and we were thus able to establish in detail how dinitrogen can be converted to ammonia in these systems. This is summed up in what has become known as the Chatt mechanism, though this gainsays the fact that it represents the cumulative efforts of many people in a large group, of which Chatt was only one, though the leader. To this day, the Chatt mechanism is the only fully characterised set of transformations of dinitrogen to ammonia [42].

The question remains as to how far this cycle reflects the dinitrogen chemistry of nitrogenases, and indeed we do not know. However, it is unlikely that the oxidation state of molybdenum (if that is essentially the active site of conventional nitrogenases) changes from zero to six during the catalytic cycle. It is not reasonable to expect
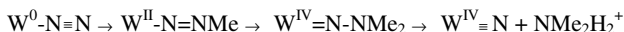
$$W^0\text{-}N{\equiv}N \rightarrow W^{II}\text{-}N{=}NH \rightarrow W^{IV}{=}N\text{-}NH_2 \rightarrow W^{IV}\text{-}N{\equiv}NH_3^+$$

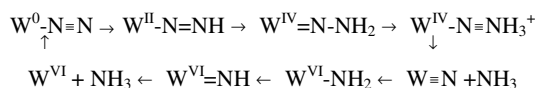$$W^{VI} + NH_3 \leftarrow W^{VI}{=}NH \leftarrow W^{VI}\text{-}NH_2 \leftarrow W{\equiv}N + NH_3$$

Fig. 6.

the reaction of a single compound of dinitrogen when exposed to acid to mimic exactly the reaction of coordinated dinitrogen in a reactive site of an enzyme where there will be controlled access of both protons and electrons. Reactions at or on an electrode surface should be a better model, as we demonstrated. Nevertheless, the dinitrogen chemistry itself was securely established by the work of the Unit of Nitrogen Fixation, and recently Schrock has produced a more sophisticated model using molybdenum and oxidation states III to VI that may well be as close to a model for nitrogenase using a single metal species as we can reasonably hope to get (Fig. 7).

Related dinitrogen protonation chemistry has been found in other systems. In particular, dinitrogen can form compounds in which it is bound to more than one metal ion, and sometimes to as many as four. Protonation under these conditions does not involve the extreme changes of oxidation state we observed originally because electrons can flow to the dinitrogen from more than one metal. We thus showed [43] that protonation of coordinated dinitrogen in Gambarotta's dinuclear vanadium(II) adduct [44] can also give rise to ammonia, but the vanadium ions are oxidised by only one unit. Thus dinitrogen plus two electrons can give rise to ammonia, perhaps because the initial step produces unstable diazene which then disproportionates (Fig. 8) [43,45].

Gambarotta's compound contains ions of two vanadium(II), each coordinated by a 2-amino-1-phenyl group. We wondered whether such a group could be replaced by a ferrocenyl derivative, in an attempt to involve a second redox-active metal centre in the dinitrogen protonation. This involved us in a lengthy study of the lithiation of a range of ferrocenyl and related amines, which turned out to be more complicated than we had expected [46]. Once bound, the ferrocenylamine groups did seem to potentiate vanadium(II) to dintrogen uptake, though the reactions were rarely clean. However, ammonia was always the product of protonation of such materials, never hydrazine.
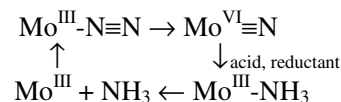
$$Mo^{III}\text{-}N{\equiv}N \rightarrow Mo^{VI}{\equiv}N$$

$$Mo^{III} + NH_3 \leftarrow Mo^{III}\text{-}NH_3 \quad \downarrow \text{acid, reductant}$$

Fig. 7. Acid: 2,6-lutidinium, reductant: decamethylchromocene.

$$W^0\text{-}N{\equiv}N \rightarrow W^{II}\text{-}N{=}NMe \rightarrow W^{IV}{=}N\text{-}NMe_2 \rightarrow W^{IV}{\equiv}N + NMe_2H_2^+$$

Fig. 5.

$$V^{II}\text{-}N{\equiv}N\text{-}V^{II} \rightarrow 2V^{III} + NH_3 + N_2$$
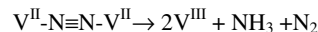
Fig. 8.

When there are four electrons available at a protonation, as with Bercaw's long-established titanium (and zirconium) systems [47] ($2 \times Ti^{II} \rightarrow 2 \times Ti^{IV}$) then hydrazine is the product. However, observations such as those from the vanadium systems keep posing the question of why Nature should use cluster systems such as in nitrogenase to generate a reactive site rather than the simpler mononuclear systems such as those we had discovered. We have yet to answer this question though it is notable that no one has yet obtained a complex in which the dinitrogen is bound to a cluster, let alone within a cluster. However, we certainly cannot exclude structures involving, for example, dinitrogen bridging between molybdenum and iron, or even between two iron atoms, as being key intermediates in the natural process. Nevertheless, it has generally been overlooked that iron alone can mediate the reduction of dinitrogen to ammonia under very mild conditions, cycling between oxidation states 0 and II.

The complex [$FeCl_2(dmpe)_2$] (dmpe=Me_2-$PCH_2CH_2PMe_2$) reacts with borohydride to give a trihydride, [$FeH_3(dmpe)_2$]$^+$, which can be isolated as a tetraphenylborate. This reacts with dinitrogen to yield a dinitrogen complex, [$FeH(N_2)(dmpe)_2$]$^+$. Treatment with base gives a complex that we have characterised in solution as [$Fe(N_2)(dmpe)_2$], though this cannot be the whole story. Treatment of our solutions of the dinitrogen complex with acids such as HCl produces ammonia and dinitrogen, and regenerates [$FeCl_2(dmpe)_2$]. This completes a cyclic system for converting dinitrogen to ammonia. Note once again that each iron atom can release only two electrons to the dinitrogen, yet ammonia is still generated [48]. In an extended study, we also determined the thermodynamics and mechanism of displacement of dihydrogen from [$FeH_3(dmpe)_2$]$^+$ and the related osmium and ruthenium complexes by nitriles and chloride [49].

We did not isolate this [$Fe(N_2)(dmpe)_2$], but [$Fe(N_2)(depe)_2$] (depe = $Et_2PCH_2CH_2PEt_2$) has since been char-acterised structurally in the solid state. However, treatment of this dinitrogen complex with HCl simply leads to [$FeCl_2(depe)_2$] and no ammonia [50], though presumably H_2. In fact, whether or not ammonia is produced in our dmpe and related systems depends on the base used to remove the proton from the (dinitrogen)hydrideiron intermediate, so that it would appear that the key is not simple [$Fe(N_2)(dmpe)_2$] but probably an adduct containing a moiety such as $Fe \leftarrow N \equiv N \rightarrow Li^+$ for which we have no direct evidence but for which there are several precedents. We leave it to others to sort this out. Notwithstanding, the system raises the possibility of a cyclic system for fixing nitrogen that is driven simply by the arrival of electrons at an iron site and a cycling of pH (Fig. 9). Such a process cannot be excluded form the possibilities open to natural systems.

Throughout our work, we have also been interested in the reactions of so-called alternative substrates for nitrogenases. Amongst these, the most interesting were alkynes and cyclopropene. The latter is something that can be prepared and stored only in rather sophisticated vacuum systems, and Charles McKenna at the University of Southern California had developed a method for doing this. He also showed [51] that nitrogenases can reduce cyclopropene stereospecifically to cyclopropane and propene, as shown by deuterium labelling, and it became of interest to discover how the reduction might occur at "model" centres. Our collaboration involved flying from Los Angeles to London clutching Dewar flasks containing ampoules of cyclopropene stored in liquid nitrogen, something that would probably not be allowed today, though the authorities at that time were very willing to help us in this matter. Using cyclopropene itself and some related more stable derivatives, we showed how these materials bond to platinum(0) and to iron(II), and we also showed that the protonation or deuteration of these model complexes competed with electronation, yielding a mixture of propenes and cyclopropanes of different stereochemistries. We were also
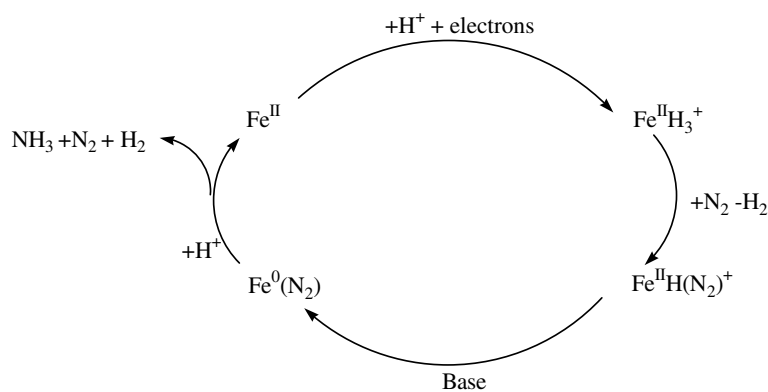

Fig. 9. A cyclic system for converting dinitrogen to ammonia, based upon a single iron centre. This cycle can be "turned" by cycling the pH, a function well within the capabilities of enzymes such as the nitrogenases.
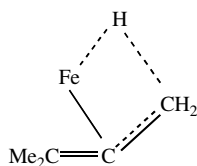
Fig. 10.

able to infer that the active site in nitrogenases must be rather acid [52,53].

Our related interest in ethynes arose from the widespread use of the reduction of ethyne itself as a test for nitrogen-fixation ability. That it is not a substrate for at least one particular kind of nitrogenase was not then appreciated. Substituted ethynes and materials such as allenes may also be nitrogenase substrates. We have investigated the reactions of such compounds with metal complexes in a variety of model systems. For example, $[FeH_3(dmpe)_2]^+$ reacts with cyclopropene to produce cyclopropane and dihydrogen, but allene and 3,3-dimethylallene, isomers of cyclopropene and 3,3-dimethylcyclopropene, form adducts in which a partially reduced allene acts as a ligand using an agostic hydrogen (Fig. 10) [52,53].

Phenylethyne and the same hydride yield a complex containing two joined acetylene residues, which can be written as PhC≡C–C=CHPh, in which only the CHPh is not also bonded to the iron. In contrast, methylethyne produces a complex with two ethynyl residues bonded η^1 and in the *trans* configuration [53]. These compounds yield hydrocarbons when treated with acids. In a related system, we have been able to isolate a cobalt complex with only one ethynyl residue bonded, *trans* to a hydride [54].

This summary of over forty years research in organometallic and dinitrogen chemistry must be somewhat subjective, but it is clear that I did not stimulate all this work myself. Serendipity played a considerable part, but the most important contribution has been from my collaborators, whose imagination, drive and insight have been the principal basis of all the progress. I have not cited the work of all of my coworkers, but to every one, whether I have cited their work or not, I owe a tremendous debt. I willingly and gratefully acknowledge it here.

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